PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : B22D 27/02	A1	(11) International Publication Number: WO 91/00158
		(43) International Publication Date: 10 January 1991 (10.01.91)

(21) International Application Number: PCT/US90/03658

(22) International Filing Date: 25 June 1990 (25.06.90)

(30) Priority data:
371,037 26 June 1989 (26.06.89) US

(71) Applicant: NRC, INC. [US/US]; 45 Industrial Place, Newton, MA 02164 (US).

(72) Inventors: BALLIETT, Robert, W. ; LILLEY, John, D. ; 45 Industrial Place, Newton, MA 02164 (US).

(74) Agents: COHEN, Jerry et al.; Perkins, Smith & Cohen, One Federal Street, Boston, MA 02110 (US).

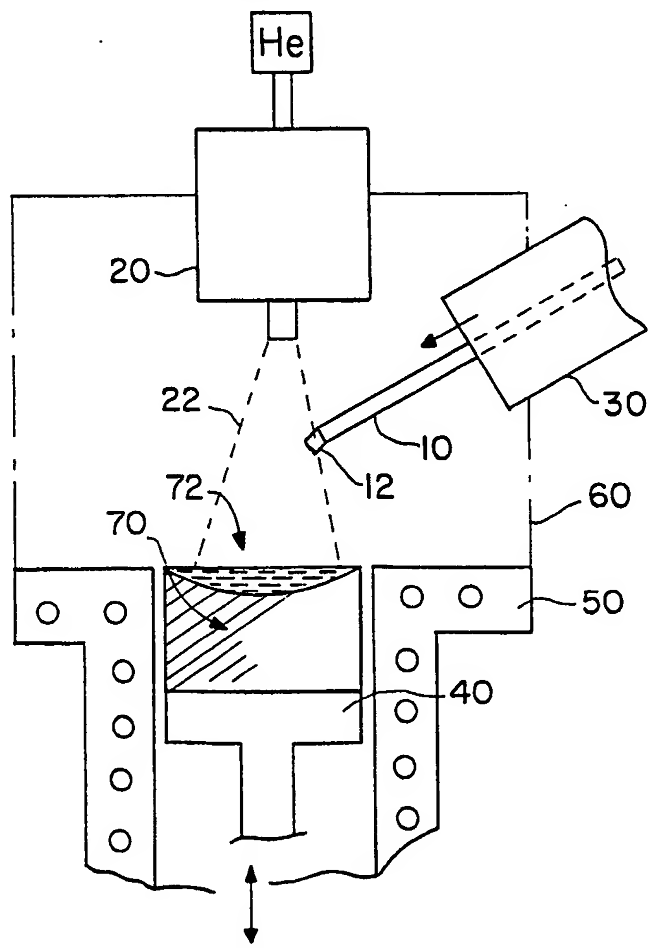
(81) Designated States: AT (European patent), AU, BE (European patent), CA, CH (European patent), DE (European patent)*, DK (European patent), ES (European patent), FR (European patent), GB (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent).

Published
With international search report.

(54) Title: PRODUCTION OF INGOTS FOR MICROCOMPOSITE MANUFACTURE BY PLASMA MELTING

(57) Abstract

Ingots from the manufacture of deformation processed composites are formed by high energy melting of interspersed metal components at high input pressure, and high rate resolidification, to produce a dispersed structure containing fine particles (1-10 microns in diameter) of one component in a matrix of the other(s). D.C. transferred arc (20) plasma melting is used for the high energy melting and superheating of a feed stock billet (10) and of an ingot melt zone (72). Electromagnetic stirring is used in homogenization of the melt. The composite can be deformed mechanically to reduce particle thickness and elongate the particles and strengthen the composite as a whole.



DESIGNATIONS OF "DE"

Until further notice, any designation of "DE" in any international application whose international filing date is prior to October 3, 1990, shall have effect in the territory of the Federal Republic of Germany with the exception of the territory of the former German Democratic Republic.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MC	Monaco
AU	Australia	FI	Finland	MG	Madagascar
BB	Barbados	FR	France	ML	Mali
BE	Belgium	GA	Gabon	MR	Mauritania
BF	Burkina Fasso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GR	Greece	NL	Netherlands
BJ	Benin	HU	Hungary	NO	Norway
BR	Brazil	IT	Italy	RO	Romania
CA	Canada	JP	Japan	SD	Sudan
CF	Central African Republic	KP	Democratic People's Republic of Korea	SE	Sweden
CG	Congo			SN	Senegal
CH	Switzerland	KR	Republic of Korea	SU	Soviet Union
CM	Cameroon	LI	Liechtenstein	TD	Chad
DE	Germany, Federal Republic of	LK	Sri Lanka	TG	Togo
DK	Denmark	LU	Luxembourg	US	United States of America

PRODUCTION OF INGOTS FOR MICROCOMPOSITE MANUFACTURE BY PLASMA MELTING

FIELD OF THE INVENTION, OBJECTS, BACKGROUND

The present invention relates to formation of metal composite systems.

Several known metal alloy systems, fiber reinforced-metal matrix composite systems and ceramic-ceramic composites have limitations that make those systems only marginally acceptable in present high temperature, high strength, high conductivity applications and in other like applications. In-situ, or deformation-processed, composites have been used in these applications with success.

It is a principal object of the invention to provide a method of production of ingots, affording optimized properties of deformation-processed composites made from the ingots.

It is another principal object of the invention to produce a dual phase ingot consisting of primary particles of one

phase in a matrix of another phase which is suitable for the manufacture of an in-situ composite. The phases may be pure metals or alloys in any combination, pure metal -pure metal, pure metal-alloy, alloy-pure metal or alloy-alloy. The term pure metal includes elements and chemical compounds of metals including inter metallic compounds and other compounds, e.g. oxides, nitrides, carbides and other ceramic forms. The terms "pure metal" and "alloy" each allow for tolerable levels of impurity inclusions. The method of production allows the controlled melting, alloying and solidification of the appropriate feed stocks into ingots for in-situ composite manufacture. The method of production allows the melting, alloying and solidification for feed stocks comprised of components with widely varying physical properties including melting temperature and vapor pressure.

SUMMARY OF THE INVENTION

The objects of the invention are realized by plasma melting as hereinafter described.

Ingots or other cast products produced by this method of production are superior to similar ingots produced by other methods due to the formation of smaller sized primary particles in the as-cast ingot. The production of these ingots with smaller primary particle sizes results in greater efficiencies in the manufacture of in-situ composites. This greater efficiency is related to a significant reduction in the total amount of cold work required to produce final product shapes having similar mechanical and physical properties compared to prior art products and processes conventionally used.

Plasma melting produces ingots for the manufacture of in-situ composites with the desired small size primary particles. The plasma melting process involves the use of a DC transferred plasma arc in an inert gas environment (at about atmospheric pressure, i.e. 0.5 -- 2.0 atmospheres) to transfer energy to the feed stock to be melted. The high energy density characteristics of the transferred arc together with the high temperatures found in the plasma gas enable the multiple components of the feed stock to melt simultaneously regardless of wide variations in melting point. The operation of the process at or above atmospheric pressure supresses the volatilization of high vapor pressure constituents, when these constitutents are superheated to abnormally high temperatures. The plasma melting process enables the use of continuously variable electromagnetic stirring of the molten pool.

An original feed stock assemblage is subjected to high power input, rapid melting (and molten material is removed therefrom, usually by gravity, to a melt collection location) to form a pool of melted-together components with the high power input contributing to rapid melting and superheating of the melt and to melt stirring. The molten pool is rapidly resolidified to achieve a new finely divided micro-composite ingot or other specifically cast product characterized by microstructure which shows a micro-composite of the original immiscible components more finely divided than in the original pre-melt assemblage, generally in the form of finely dispersed dendrites or spheroids of one to ten microns average diameter, of the higher melting point component in a matrix of the lower melting point component(s). The ingot, or the like, so produced by this initial melting can be remelted by conventional arc or electron beam melting of the ingot itself. Such remelt can be at low temperature to form castings having structures similar to highly worked material.

The high input power melting for deformation-processed composite ingot formation is preferrably achieved by d.c. transferred arc, plasma torch melting and preferrably in operation at superatmospheric pressure, inert gas environments to limit vaporizing, at the surface of the melt, of any of the melt components.

After melting and resolidification the composite is deformed in a high force, high strain process such as rolling or drawing.

The end material results of the foregoing processing (in the as-cast or as-worked conditions) provide substantial departures from prior art limitations on materials properties. For example, the conventional copper-beryllium alloys used in high temperature aerospace, electrical and electronic applications (despite known drawbacks of cost, weight and production problems, including toxicity) can be replaced by a niobium-copper deformation-processed composite material system of the present invention in a five to thirty weight percent of niobium, balance essentially copper, with a microstructure of less than one micron thickness ribbons or filaments of niobium in the copper matrix after deformation of the ingots as described above. The unusual strengths of these composites while maintaining high conductivity reflect favorable variances relative to a Law of Mixtures projection at each percentage in the ratio range given. Further the niobium-copper microcomposite series includes several alloy systems superior to conventional beryllium-copper alloys in high temperature conductivity and strength, to an extent enabling production of mill products (e.g., wire) with the new micro-composite system equivalent in properties to the old alloy system with a substantial weight saving on the order of fifty percent.

Similar substitution of the new micro-composite systems for traditional metal alloy and element systems, and even for certain ceramic systems, can yield improved brake and clutch systems, motor windings, heat exchanges, electrical arc contacts, connectors, brushes for motors and generators. In many of these applications improved contact erosion resistance can be achieved through the new systems.

As noted above, substantial production advantages are also achieved through the invention in that the extent of cold working from cast to final product shape can be reduced while producing the desired microstructure and target physical properties in the final product. Production advantages are also realized through the invention's close control of gross composition and of uniformity of distribution of desired composition, phases and crystal sizes within the final product.

Other objects, features, and advantages will be apparent from the following detailed description of preferred embodiments taken in conjunction with the accompanying drawings in which:

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross-section view of an initial assemblage lay-out, as described above, as applied to a niobium-copper system;

FIGS. 2-3 are cross-section views in two embodiments of a melt pool surrounded by schematically shown elements of the melt processing system (using a single plasma torch for feed melt and crucible power input in FIG. 2 and multiple torches in FIG. 3);

FIGS. 4 - 5 are top views of molten pools showing plasma beam deflection at the pool surface (by deflecting a gimbal-mounted plasma torch per se);

FIGS. 6, 7 and 8 are SEM-photomicrographs (1,000X) of structures of materials (of final ingots) made through practice of the method of the invention in certain embodiments; and

FIGS. 9-10 are plots of strength vs. diameter (FIG. 9) and electrical conductivity vs. diameter (FIG. 10) of wire produced from ingots of the photomicrographs.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

Ingots are preferrably formed by melting composite bars of the desired constituents in a transferred d.c. plasma arc and collecting and solidifying the molten metal in a collection crucible or the like, in a controlled manner. Other methods of providing the feed stock to the molten pool could also be used. Both components of the feed stock could be provided in granular form and continuously fed into the crucible by various configurations including weigh feeders. The components could be provided in the form of a pressed bar made from powders of the components. Alternatively one or more of the components can be introduced to the crucible in the form of a liquid metal.

The composite bars for melting are formed by asssembling multiple components of the appropriate constitutents in the same ratio as in the desired ingot. The basis for the ratio may be either volume or weight percent. The individual components of the assemblage may be any form or combination of bars, sheet, rod, wire, granules, or powder. The components of each of the constituents are interspersed with one another to form a relatively uniform distribution of constituents along the length, width and thickness of the bar. This assemblage is compressed to provide good contact between the individual components and may be welded together. This bar is then melted in a transferred plasma arc in a furnace containing an inert gas atmosphere. The pressure within the furnace chamber will vary with the material system being melted. In normal operation, the furnace pressure will always be greater than or equal to one atmosphere. However, there may be material systems in which melting could be done at sub-atmospheric pressures. The melting process begins by establishing a molten pool in the withdrawal crucible. Prior to the melt, a stump of the material to be melted is installed on

the end of the ingot withdrawal cylinder. The stump is then positioned in the withdrawal crucible so that its top is at the desired level of the liquid metal in the crucible. The stump in this position seals the bottom of the crucible. The arc is struck and directed at the stump. As the stump is heated, the top portion of the stump becomes molten while the bottom portion remains solid and mechanically attached to the ingot withdrawal cylinder. The molten stump forms the initial molten pool.

The composite bar then is fed mechanically into the space over the crucible. The transferred plasma arc is maintained alternately between the composite bar and the molten pool and the crucible. When the plasma torch directs the arc at the composite bar, the bar melts and the resulting molten metal drips into the crucible. The molten pool is maintained in the crucible by the intermittent application of the arc to the pool. As liquid metal is added to the pool, the stump is withdrawn to maintain the liquid level in the crucible. The ingot is formed by the solidification of the molten pool as the ingot is withdrawn.

The solidification of the molten pool is controlled through the adjustment of power input to the pool, crucible design, the application of electromagnetic stirring, cooling water flow rate and the withdrawal rate. The power input to the pool is controlled through the adjustment of arc residence time on the pool in a single torch operation. In a multi-torch operation, the current level of the torch on the pool can be varied independently to control power input. The electrmagnetic stirring current can be varied or continuous in either direction reinforcing or suppressing motion imparted to the pool by the momentum of the gas flow from the plasma torch. Some motion in the pool is generated by momentum transfer from the torch gas to the liquid metal. The withdrawal rate is continuously variable

from zero up to the maximum melt rate attainable for a given material at a given power level.

The power distribution over the melt stock and the molten pool is controlled by the motion of the plasma torch. The torch or torches can be gimbal mounted or otherwise mounted with multi-axix movement capability for X, Y, Z motion of a torch nozzle and emergent plasma. The torch or torches are preferrably hydraulically operated and moved in regular patterns which are repeated periodically to optionally distribute the power from the transferred plasma arc among the feedstock to be melted and the melt at the top of the crucible. The torch patterns, as defined by the geometric forms tracked by the point of impact of the arc take the forms of ellipses, points, lines, circles, or a combination of forms in series. The power distribution is determined, and the torch patterns are selected based upon visual observation during the melt, and the evaluation of the ingot structure subsequent to the melt.

FIG. 1 shows an initial assemblage 10 of rectangular solid form (typically sixty inches length (l), eight inches height (h), eight inches width (w), with alternating w/h rectangular layers of niobium (Nb) and copper (Cu) - respectively, .20" and .060" inches thick typically in the l dimension for forming a five - thirty (Nb-Cu) weight percent composite.

FIG. 1A shows a similar assemblage 10A with twin l/w rectangles of the components interspersed in an h-dimension array.

Other assemblages can be formed, as shown for example in FIG. 1B where a similar rectangular bar is made up from component bars of differing orientations of the thin component layers.

Cylindrical, elliptical, cruciform or irregular cross-section billets can replace the rectangular assemblages of FIGS. 1, 1A, 1B. Concentric or pie wedge arrays can also be provided. Generally powder masses are less preferred as initial assemblage; but powder metallurgy produced disks can be used as component layers.

The components need not be in simple A-B-A-B-A-B thicknesses. Staggered arrays of uniform thickness elements can be used for ratio control, e.g., A-B-B-A-B-B-A...; A-A-B-B-B-A-A-B-B-B-...; A-A-B-A-A-B-A-A...;etc. Differing thicknesses of components can be provided rather than uniform thicknesses.

The assemblage can be made by coating using various coating methods -- including electroplating, plasma spraying, sputtering, vacuum deposition, casting, plasma vapor deposition, electropheresis and other known coating technologies to avoid cladding problems of certain materials. This approach is particularly useful for chrome-copper composites. A layer of chrome of five to fifteen mils can be deposited on a sheet of copper which is three to six times coating thickness and cut into short sections which are stacked as described above.

FIG. 2 shows an apparatus for processing the billet assemblages 10, or the like and comprises a plasma torch system 20 of known form per se (e.g., as described in the article: "Plasma Torches and Plasma torch Furnaces" by R.C. Eschenbach et ali., appearing as Chapter 7 of the book, Plasma Technology In Metallurgical Processing (published by Iron and Steel Society, Warrendale, Pa., U.S.A., 1987), a billet feeder 30, an arc-melt type removable mold stool 40 surrounded by a water cooled mold assembly. An enclosure 60 is indicated and comprises vacuum pumping and inert gas backfill equipment (not shown). The ingot 70

formed by drops melted at the billet collected in pool 72 and solidified as stool 40 is pulled downwardly. The assembled feed billet can be on the order of half a foot to several feet long and have a useful area ranging from about ten square inches to about one hundred square inches The atmospheric or superatmospheric pressure condition of the enclosure suppresses volatilization. The torch is designed to accommodate such pressure.

The plasma column 22 can be diverted to end 12 of the billet 10, to pool 72 or to both. The area as well as the direction of the gas column can be controlled.

While a variety of plasma conditions may be utilized consistent with the invention, preferred practice has comprised initial evacuation of the melt enclosure to less than ten microns with sufficient integrity of the vacuum enclosure that rate of rise from such level is less than 10 microns per minute, then back filling with helium to 740 mm Hg., then a second pump down to 50 microns and a final backfill with helium to the operating pressure. If desired, argon can be substituted for helium. The plasma torch operates with a helium or argon flow through the torch, a power input of 250 kw to 3 megawatt is provided for the torch and this translates to an effective power input of fifty KW to two hundred fifty KW per square inch of surface area of heated metal zone at the melt zone surface in the crucible (and a similar specific power imput when the torch is aimed at the feed stock) moving at a rate of two to ten inches per second.

FIG. 3 shows an apparatus similar to FIG. 2, but using multiple transferred arc plasma torch systems 20A and 20B for pool and feed heating, respectively.

FIGS. 4 and 5 show molten pools 72-4 and 72-5, respectively, with plasma column traces 22-4 and 22-5 applied thereto in oscillating patterns. These comprise a sinusoidal trace and flyback return in FIG. 4 and a continuous annular path in FIG. 5. The torch is mounted on gimbals and deflected by hydraulic pneumatic or electrical motor drives not shown to change the plasma in direction for such trace or path movement.

The practice of the invention is further illustrated by the following non-limiting examples of practice thereof.

Example 1

(a) A furnace was set up as shown in FIG. 2. Feedstock billets of the form shown in FIG. 1 were prepared using 5 weight percent (w/o) niobium, balance copper, with low impurity levels (i.e. reactor grade niobium, OFHC grade copper). The dimensions of overall feed stock billets were 3" x 2.5" x 60". The niobium component was in the form of .020" thick strips and the copper was in the form of .060" thick strips. The furnace evacuation and backfill conditions were as described above using helium. Melt and resolidification processing was as described above and elaborated in Tables I and II below. An eight inch diameter melt crucible was used to produce ingots of approximately 36" in length.

Table I - Process Conditions

(a) Gas Environment Control. The furnace was evacuated to a pressure of eight microns with a rate of rise of two microns/minute. The furnace was backfilled with helium to a pressure of fifty microns. The furnace was then backfilled again to a pressure of 800 torr to begin melting.

(b) Melting was performed using a Retech RP250T d.c. transferred arc plasma torch operating at 180 volts at a current of 1,500 amperes. Helium was supplied to the torch at 60 psi at a flow rate of 28SCFM. A torch pattern that generated a three inch diameter circle centered on the crucible center line was used.

(c) Electromagnetic Stirring.

A stirring current of one hundred amperes was used in a stirring coil approximately twelve inches in diameter surrounding the withdrawal crucible. Polarity was selected so that the electromagnetic stirring reinforced the motion imparted to the molten metal by momentum transfer from the plasma gas.

Table II

(a) Ingot Chemical Analysis

The chemical analysis of the ingot produced in Example I is as follows:

Nb	O	N	C	S	H	Cu
(wt %)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	
5.1%	91	8	18	5	1	Balance

(b) Ingot Structure

The ingot produced was examined metallographically to measure the size of the niobium particles. The average particle size was 0.97 microns. A representative photomicrophaph is shown in FIG. 6.

(c) Mechanical Properties

The ingot produced was hot extruded at a temperature of 1,400'F to a one inch diameter rod and cole drawn to 0.002" diameter wire. The ultimate tensile strength is shown as a function of wire size in FIG. 9. The electrical conductivity of the wire was measured; as shown as a function of wire size in FIG. 10.

Example II

A copper -12 weight percent niobium feedstock assemblage was processed as in Example I. The ingot produced was characterized as described in Table III below.

Table III

(a) Ingot Chemical Analysis

The chemical analysis of the ingot produced in Example II is as follows:

Nb	O	N	C	S	H	Cu
(wt %)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	

11.8%	123	19	42	7	1	Balance

(b) Ingot Structure

The ingot produced in Example II was examined metallographically to measure the size of the niobium particles. The average particle size was found to be 1.40 microns. A representative photomicrograph is shown in FIG. 7.

(c) Mechanical Properties

The ingot produced in Example II was hot extruded at a temperature of 1,400'F to a one inch diameter rod and cold drawn to 0.002" diameter wire. The ultimate tensile strength of this wire is shown as a function of wire size in FIG. 9. The electrical conductivity of the wire was measured, it is shown as a function of wire size in FIG. 10.

Example III

A copper -18 weight percent niobium feedstock assemblage was processed as in Example I. The ingot produced was characterized as described in Table IV below.

Table IV

Nb	O	N	C	S	H	Cu
(wt %)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	
17.7%	258	70	32	10	4	Balance

(b) Ingot Structure

The ingot produced in Example III was examined metallorgraphically to measure the size of the niobium particles. The average particle size was found to be 1.45 microns. A representative photomicrograph is shown in FIG. 8.

(c) Mechanical Properties

The ingot produced in Example III was hot extruded at a temperature of of 1,400'F to a one inch diameter rod and subsequently cold drawn to 0.002" diameter wire. The ultimate tensile strength of this wire is shown as a function of wire size in FIG. 9. The electrical conductivity of the wire was measured; it is shown as a function of wire size in FIG. 10.

It will now be apparent to those skilled in the art that other embodiments, improvements, details, and uses can be made consistent with the letter and spirit of the foregoing disclosure and within the scope of this patent, which is limited only by the following claims, construed in accordance with the patent law, including the doctrine of equivalents.

What is claimed is:

CLAIMS

1. Method of making ingots for the production of deformation processed composites comprising:

(a) forming an assemblage of interspersed multiple metal components of a system of at least two components,

(b) melting and then resolidifying, portions of the assemblage to form a cast product, the melting being conducted at a pressure of at least 100 mm Hg. to suppress volatilization of components and at a high energy input rate using a plasma arc, and the resolidification rate being controlled to produce a finely divided structure, with the gross composition of the cast product being essentially the same as that of the assemblage, whereby a composite is formed with fineness of reinforcing particle size and purity, substantially improved relative to arc melted or powder metallurgy materials.

2. Method in accordance with claim 1 wherein the external energy source is a d.c. transferred plasma arc.

3. Method in accordance with claim 1 and further comprising the step of stirring the melt for homogenization therein.

4. Method in accordance with claim 1 wherein the assemblage and melt zone are alternately heated by an external energy source.

5. Method of claim 1 in combination with the step of deformation-processing the ingot to enhance the strength of the cast product.

6. A product as made by the process of claim 1.

7. A micro-composite product with sub-micron particles of a first material in a matrix of a second material of lower melting point than the first material, as made by interspersing of the two materials and rapidly melting and resolidifying the interspersed materials under conditions to preserve starting composition (i.e., suppress volatilization of the first and second materials and limit contamination) and maintain and enhance uniformity of dispersion of the first material in the second and limit grain growth, the microcomposite product being workable to elongate the particles of the first material into sub-micron thickness ribbons or filaments.

8. The product of claim 7 wherein the first material is niobium and the second material copper.

9. The product of claim 8 wherein the niobium comprises five to thirty weight percent of the combined niobium and copper.

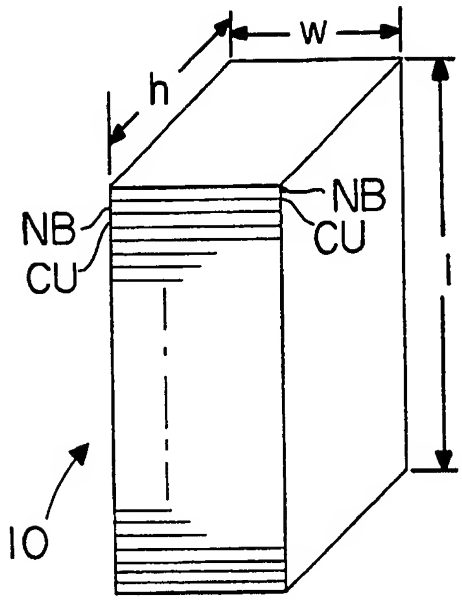


FIG. 1

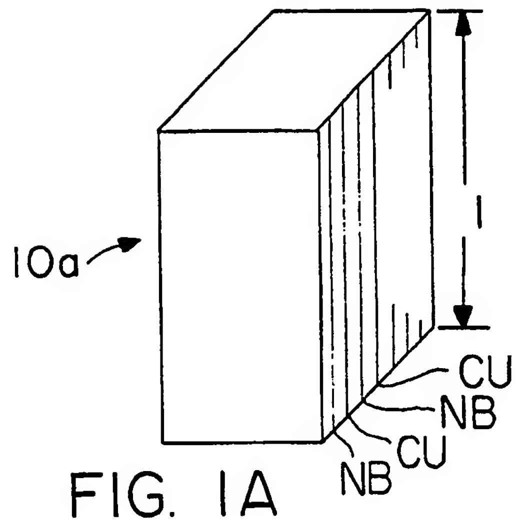


FIG. 1A

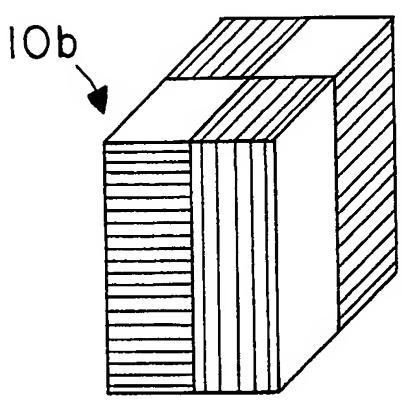


FIG. 1B

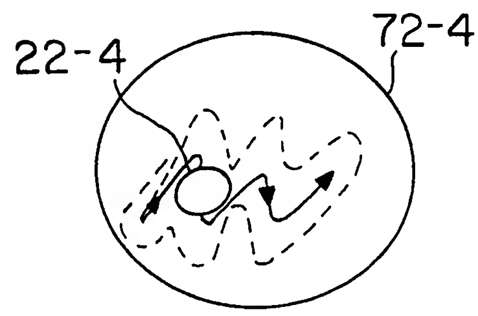


FIG. 4

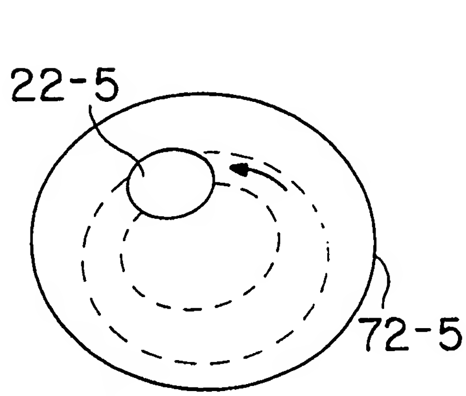


FIG. 5

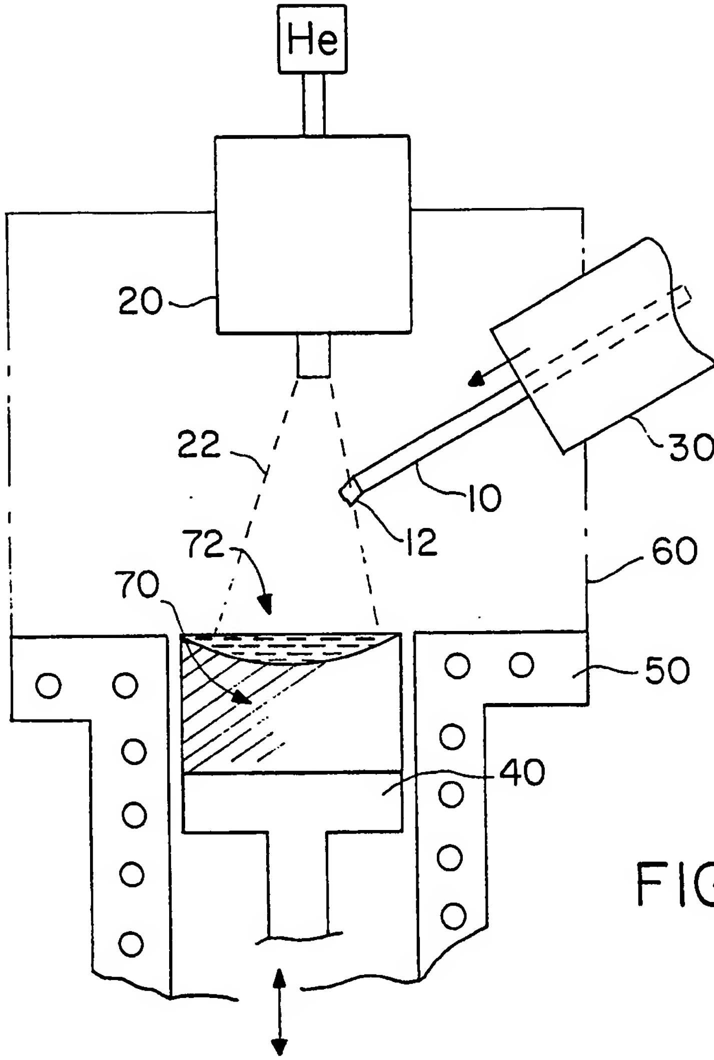


FIG. 2

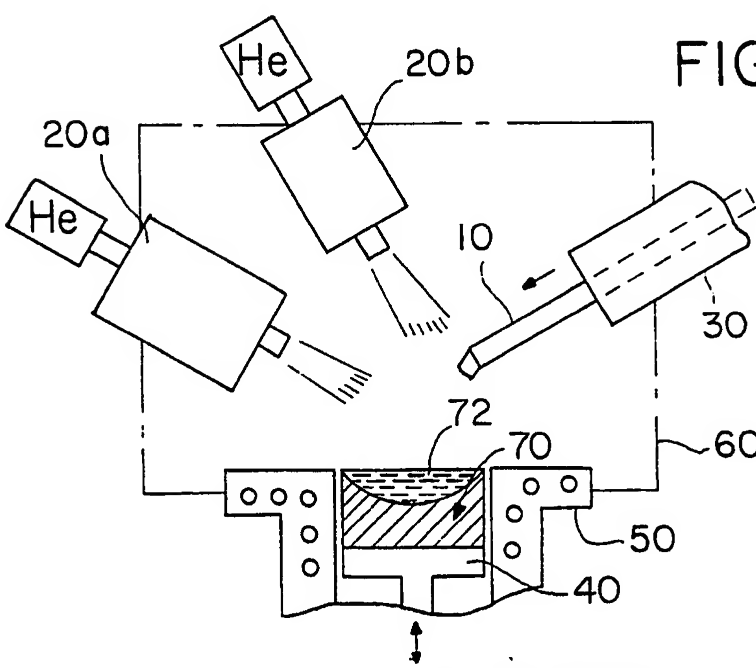


FIG. 3

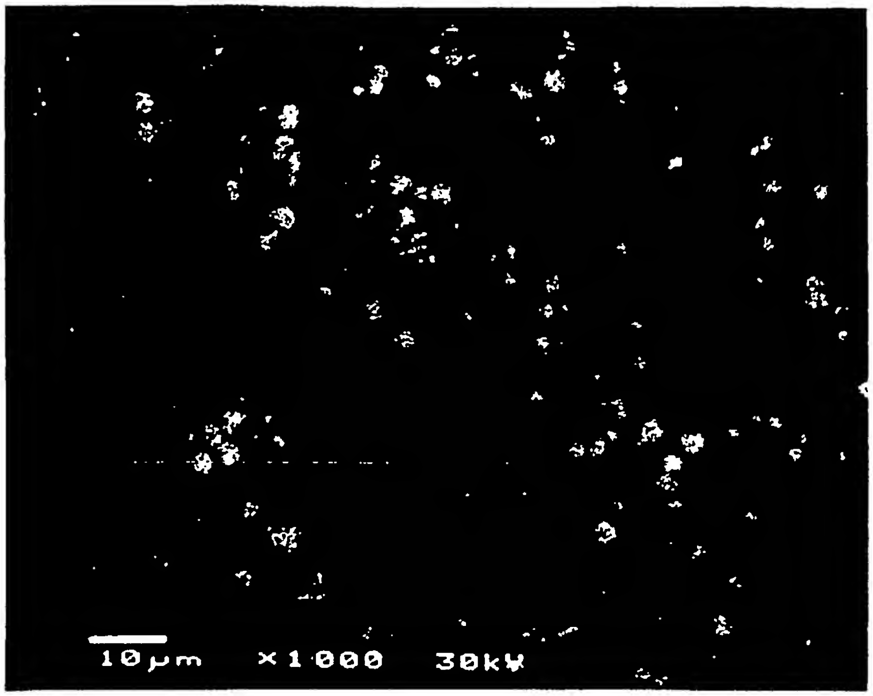


FIG.6

CU-5%NB

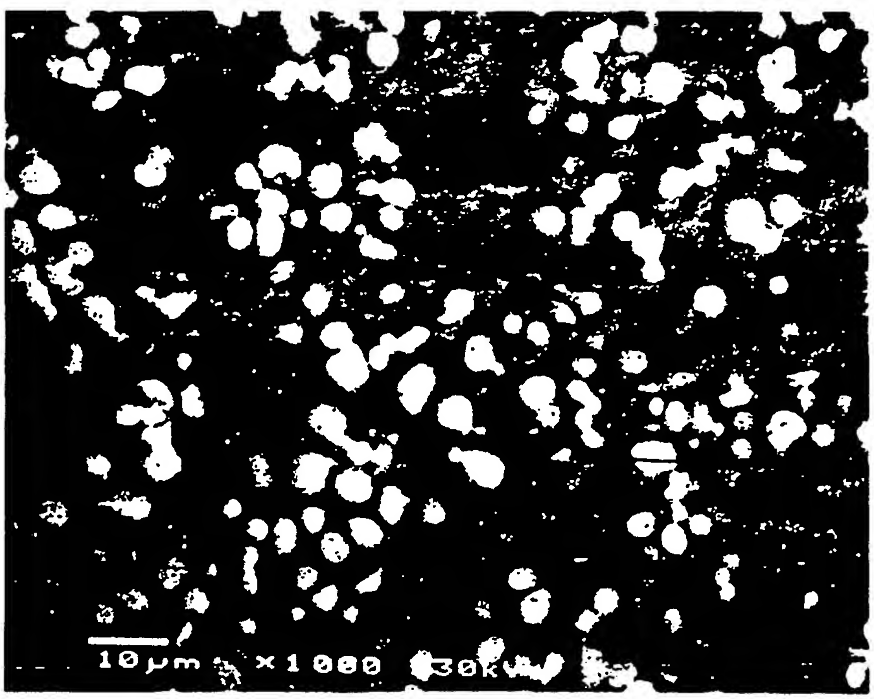
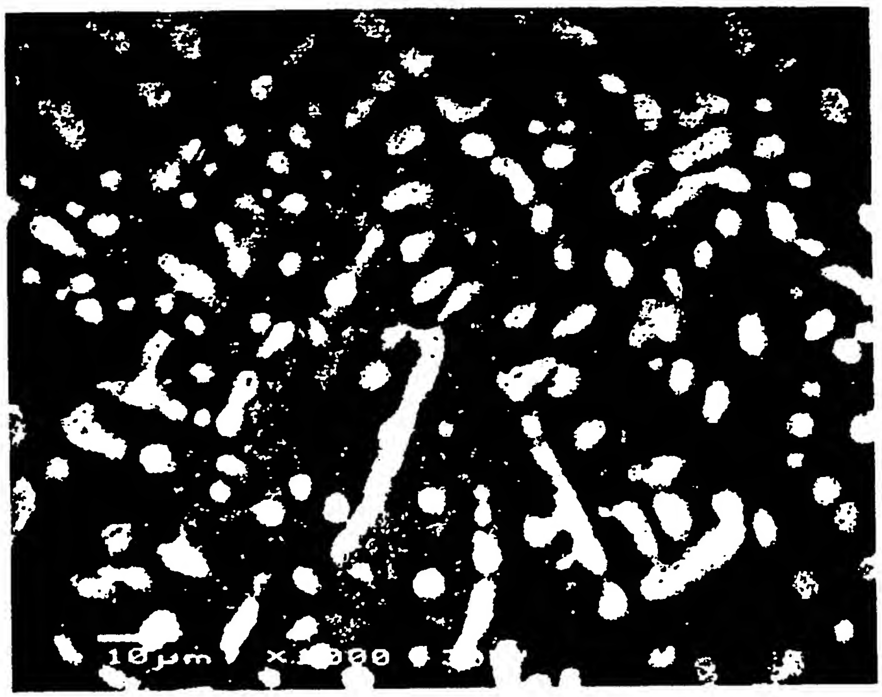


FIG.7

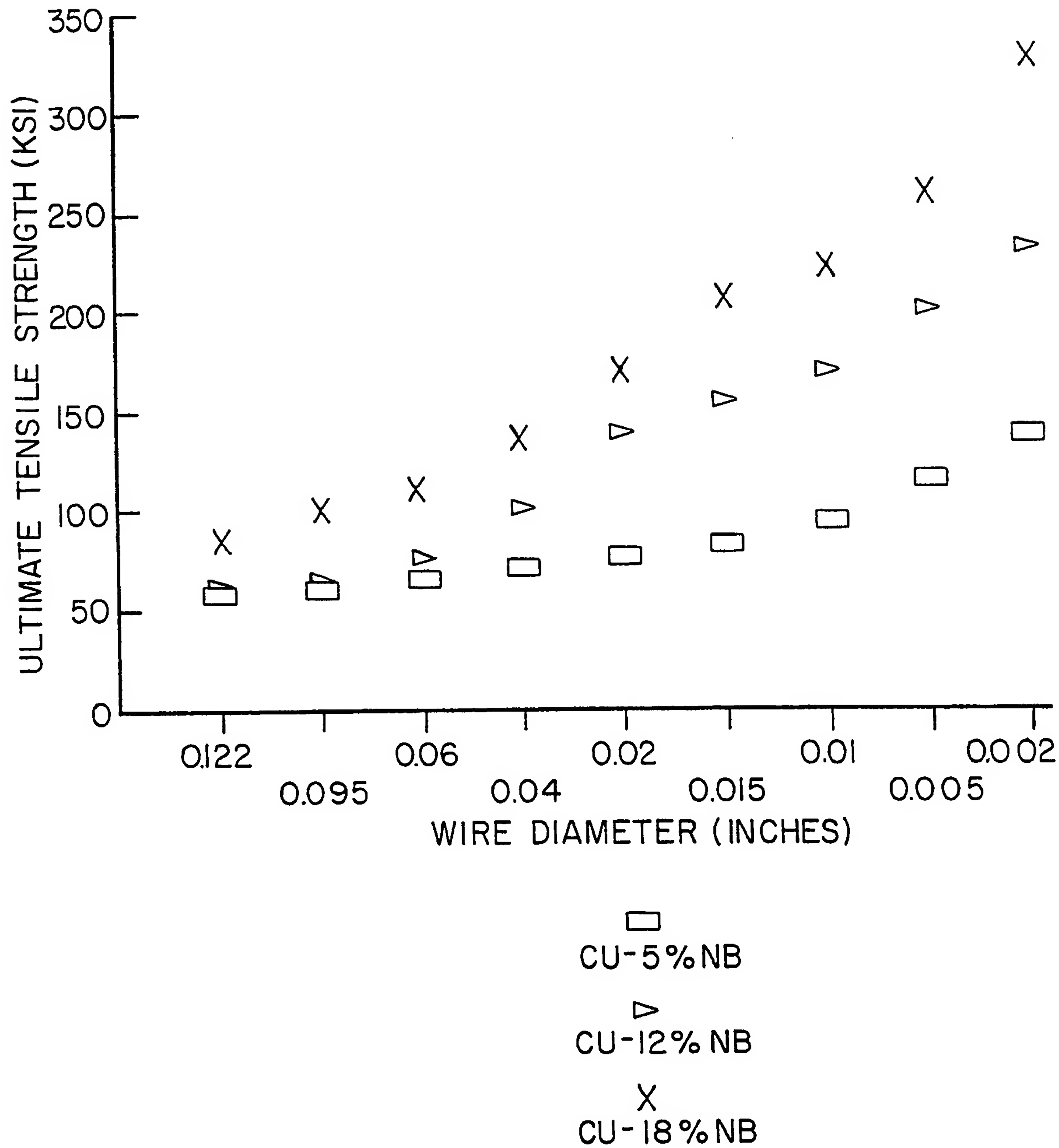
CU-12% NB



CU-18% NB

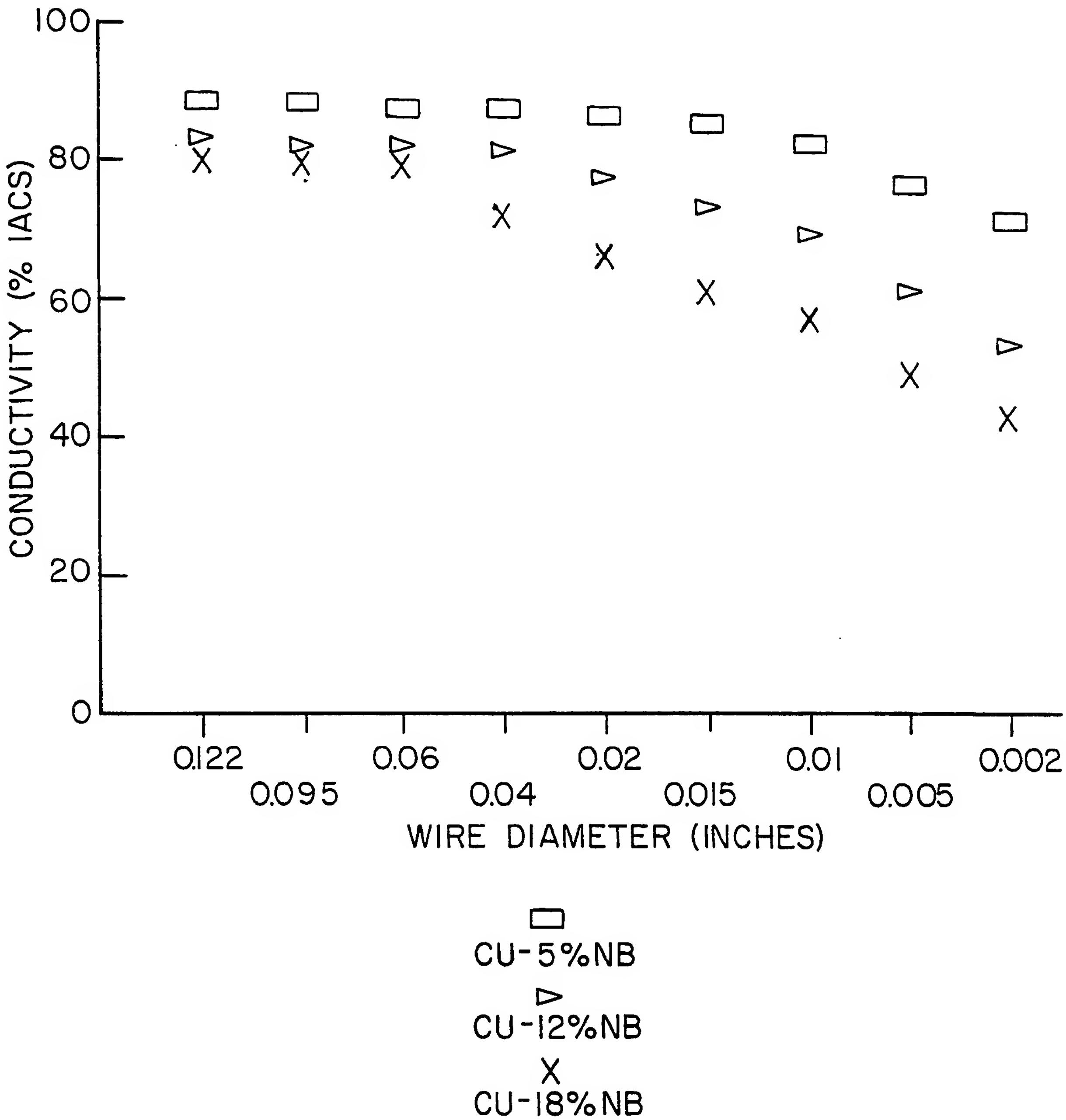
FIG. 8

FIG. 9



ULTIMATE TENSILE STRENGTH (KSI)
350
300
250
200
150
100
50
0
0.122
0.095
0.06
0.04
0.02
0.015
0.01
0.005
0.002
WIRE DIAMETER (INCHES)
CU-5% NB
CU-12% NB
CU-18% NB

FIG. 10


100
80
60
40
20
0
CONDUCTIVITY (% IACS)
0.122
0.095
0.06
0.04
0.02
0.015
0.01
0.005
0.002
WIRE DIAMETER (INCHES)
CU-5%NB
CU-12%NB
CU-18%NB

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US90/03658

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC (5): B22D 27/02

U.S. Cl. 164/469, 496

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
U.S.	164/469,495

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
X	US, A, 4,610,296 (HIRATAKE et al.) 09 September 1986 (See the entire document)	1-5
Y	US, A, 4,017,672 (PATON et al.) 12 April 1977 (Note Figure 1)	1-5
Y	US, A, 3,894,573 (PATEN et al.) 15 July 1975 (Note Figures 2 and 3)	1-5
A	JP, A, 55-6089 KOBE STEEL, 13 February 1980	

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
22 August 1990	18 OCT 1990
International Searching Authority	**Signature of Authorized Officer**
ISA/US	R. Pelto

International Application No. PCT/US90/03652

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE [1]

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers , because they relate to subject matter [1] not required to be searched by this Authority, namely:

2. ☐ Claim numbers , because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out [1], specifically:

3. ☐ Claim numbers___________, because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☒ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING [2]

This International Searching Authority found multiple inventions in this international application as follows:

I. Claims 1-5, Drawn to a method of making ingots, classified in class 164, subclass 76.1

II. Claims 6-9 drawn to a micro-composite product, classified in class 428, subclass 615.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

   1-5 (Telephone practice)

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.